

ORIGINAL

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## ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES

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## **ORGANIC ELEMENT FOR ELECTROLUMINESCENT DEVICES**

### **FIELD OF THE INVENTION**

This invention relates to an electroluminescent device comprising a cathode, an anode, and located therebetween a light emitting layer (LEL)

5 containing (1) a host material that comprises a N,N,N',N'-tetra-aromatic benzidine group substituted in at least one position ortho to the biphenyl linkage between the phenyl groups of the benzidine nucleus and (2) a phosphorescent light emitting material, wherein the triplet state energy of the benzidine nucleus is higher than the triplet state energy of the phosphorescent emitting material.

### **BACKGROUND OF THE INVENTION**

10 While organic electroluminescent (EL) devices have been known for over two decades, their performance limitations have represented a barrier to many desirable applications. In simplest form, an organic EL device is comprised of an anode for hole injection, a cathode for electron injection, and an organic  
15 medium sandwiched between these electrodes to support charge recombination that yields emission of light. These devices are also commonly referred to as organic light-emitting diodes, or OLEDs. Representative of earlier organic EL devices are Gurnee et al. U.S. Pat. No. 3,172,862, issued Mar. 9, 1965; Gurnee U.S. Pat. No. 3,173,050, issued Mar. 9, 1965; Dresner, "Double Injection  
20 Electroluminescence in Anthracene", RCA Review, Vol. 30, pp. 322-334, 1969; and Dresner U.S. Pat. No. 3,710,167, issued Jan. 9, 1973. The organic layers in these devices, usually composed of a polycyclic aromatic hydrocarbon, were very thick (much greater than 1  $\mu\text{m}$ ). Consequently, operating voltages were very high, often >100V.

25 More recent organic EL devices include an organic EL element consisting of extremely thin layers (e.g. <1.0  $\mu\text{m}$  ) between the anode and the cathode. Herein, the term "organic EL element" encompasses the layers between the anode and cathode electrodes. Reducing the thickness lowered the resistance of the organic layer and has enabled devices that operate much lower voltage. In a  
30 basic two-layer EL device structure, described first in US 4,356,429, one organic

layer of the EL element adjacent to the anode is specifically chosen to transport holes, therefore, it is referred to as the hole-transporting layer, and the other organic layer is specifically chosen to transport electrons, referred to as the electron-transporting layer. Recombination of the injected holes and electrons within the organic EL element results in efficient electroluminescence.

There have also been proposed three-layer organic EL devices that contain an organic light-emitting layer (LEL) between the hole-transporting layer and electron-transporting layer, such as that disclosed by Tang et al [*J. Applied Physics*, Vol. 65, Pages 3610-3616, 1989]. The light-emitting layer commonly consists of a host material doped with a guest material. Still further, there has been proposed in US 4,769,292 a four-layer EL element comprising a hole-injecting layer (HIL), a hole-transporting layer (HTL), a light-emitting layer (LEL) and an electron transport/injection layer (ETL). These structures have resulted in improved device efficiency.

Many emitting materials that have been described as useful in an OLED device emit light from their excited singlet state by fluorescence. The excited singlet state is created when excitons formed in an OLED device transfer their energy to the excited state of the dopant. However, it is generally believed that only 25% of the excitons created in an EL device are singlet excitons. The remaining excitons are triplet, which cannot readily transfer their energy to the singlet excited state of a dopant. This results in a large loss in efficiency since 75% of the excitons are not used in the light emission process.

Triplet excitons can transfer their energy to a dopant if it has a triplet excited state that is low enough in energy. If the triplet state of the dopant is emissive it can produce light by phosphorescence, wherein phosphorescence is a luminescence involving a change of spin state between the excited state and the ground state.. In many cases singlet excitons can also transfer their energy to lowest singlet excited state of the same dopant. The singlet excited state can often relax, by an intersystem crossing process, to the emissive triplet excited state.

Thus, it is possible, by the proper choice of host and dopant, to collect energy from

both the singlet and triplet excitons created in an OLED device and to produce a very efficient phosphorescent emission.

One class of useful phosphorescent materials are transition metal complexes having a triplet excited state. For example, *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III) (Ir(ppy)<sub>3</sub>) strongly emits green light from a triplet excited state owing to the large spin-orbit coupling of the heavy atom and to the lowest excited state which is a charge transfer state having a Laporte allowed (orbital symmetry) transition to the ground state (K.A. King, P.J. Spellane, and R.J. Watts, *J. Am. Chem. Soc.*, **107**, 1431 (1985), M.G. Colombo, T.C. Brunold, T. Reidener, H.U. Gudel, M. Fortsch, and H.-B. Burgi, *Inorg. Chem.*, **33**, 545 (1994) Small-molecule, vacuum-deposited OLEDs having high efficiency have also been demonstrated with Ir(ppy)<sub>3</sub> as the phosphorescent material and 4,4'-N,N'-dicarbazole-biphenyl (CBP) as the host (M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, *Appl. Phys. Lett.*, **75**, 4 (1999), T. Tsutsui, M.-J. Yang, M. Yabuchi, K. Nakamura, T. Watanabe, T. Tsuji, Y. Fukuda, T. Wakimoto, S. Miyaguchi, *Jpn. J. Appl. Phys.*, **38**, L1502 (1999)).

Another class of phosphorescent materials include compounds having interactions between atoms having d<sup>10</sup> electron configuration, such as Au<sub>2</sub>(dppm)Cl<sub>2</sub> (dppm = bis(diphenylphosphino)methane) (Y. Ma et al, *Appl. Phys. Lett.*, **74**, 1361 (1998)). Still other examples of useful phosphorescent materials include coordination complexes of the trivalent lanthanides such as Tb<sup>3+</sup> and Eu<sup>3+</sup> (J. Kido et al, *Appl. Phys. Lett.*, **65**, 2124 (1994)). While these latter phosphorescent compounds do not necessarily have triplets as the lowest excited states, their optical transitions do involve a change in spin state of 1 and thereby can harvest the triplet excitons in OLED devices.

The light-emitting layer in an efficient electroluminescent device commonly consists of a host material doped with a phosphorescent guest material. Suitable hosts for phosphorescent materials should be selected so that the triplet exciton can be transferred efficiently from the host material to the phosphorescent material. Examples of host materials are described in WO

00/70655 A2; 01/39234 A2; 01/ 93642 A1; 02/074015 A2; 02/15645 A1, US 20020117662, and US 2003157366.

Notwithstanding these developments, there remains a need for new organic materials that will provide useful light emissions and function as hosts for phosphorescent materials having improved efficiency, stability, manufacturability,  
5 or spectral characteristics.

### **SUMMARY OF THE INVENTION**

The invention provides an electroluminescent device comprising a cathode, an anode, and located therebetween a light emitting layer (LEL)  
10 containing (1) a host material that comprises a N,N,N',N'-tetra-aromatic benzidine group substituted in at least one position ortho to the biphenyl linkage between the phenyl groups of the benzidine nucleus and (2) a phosphorescent light emitting material, wherein the triplet state energy of the benzidine nucleus is higher than the triplet state energy of the phosphorescent emitting material. The invention  
15 also provides a display and an area lighting device and a process for emitting light.

The invention provides useful light emissions.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 shows a cross-section of a typical OLED device in which this invention may be used.

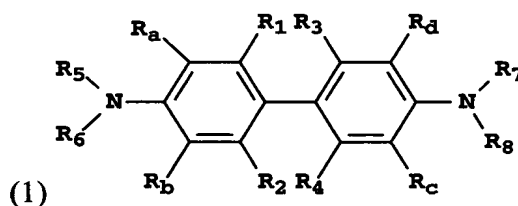
### **DETAILED DESCRIPTION OF THE INVENTION**

20 The invention provides an electroluminescent device comprising a light-emitting layer that contains an organic material comprising a substituted benzidine compound. A benzidine compound of the invention consists of a biphenyl moiety, formed by linking two benzene groups, that are substituted in the  
25 4,4' positions with N,N,N',N'-tetra-aromatic amino groups. A benzidine compound that is useful for the practice of this invention has at least one substituent ortho to the biphenyl linkage. In one desirable embodiment, the benzidine compound has two or more substituents ortho to the biphenyl linkage. The ortho substituent(s) is chosen so that the biphenyl group is prevented from

becoming co-planar in the lowest triplet state of the molecule, thereby raising the energy of this state. The twisted benzidine compound has a high-energy triplet state and may be a suitable host for blue, green, and red phosphorescent dopants. Without such substitution, most benzidine compounds have triplet energies too low to be useful for this application, especially in the case of blue and green phosphorescent dopants.

In one desirable embodiment, the benzidine compound of the invention can be represented by Formula (1), provided that  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  comprise at least one independently selected substituent other than hydrogen.

Examples of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are a halogen group, such as fluoro, a methyl group and a phenyl group.  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  represent aromatic groups, provided that the substituents represented by  $R_5$  and  $R_6$ , and  $R_7$  and  $R_8$  do not join to form a ring. Examples of  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are phenyl ring groups, tolyl ring groups, biphenyl ring groups.  $R_a$ ,  $R_b$ ,  $R_c$  and  $R_d$  represent hydrogen or a substituent.



In Formula (1), it is desirable that  $R_1$ - $R_8$  and  $R_a$ - $R_d$  be chosen so that the triplet state energy of the benzidine material is higher than the triplet state energy of the phosphorescent emitting material. Suitable  $R_1$ - $R_8$  and  $R_a$ - $R_d$  substituents can be determined by calculating the triplet energy of the host of Formula (1) containing these substituents. This calculated triplet energy should be higher than that of the calculated triplet energy of the phosphorescent light emitting material.

The triplet state energy for a molecule is defined as the difference between the ground state energy ( $E_{gs}$ ) of the molecule and the energy of the lowest triplet state ( $E_{ts}$ ) of the molecule, both given in eV. These energies can be calculated using the B3LYP method as implemented in the Gaussian98

(Gaussian, Inc., Pittsburgh, PA) computer program. The basis set for use with the B3LYP method is defined as follows: MIDI! for all atoms for which MIDI! is defined, 6-31G\* for all atoms defined in 6-31G\* but not in MIDI!, and either the LACV3P or the LANL2DZ basis set and pseudopotential for atoms not defined in MIDI! or 6-31G\*, with LACV3P being the preferred method. For any remaining atoms, any published basis set and pseudopotential may be used. MIDI!, 6-31G\* and LANL2DZ are used as implemented in the Gaussian98 computer code and LACV3P is used as implemented in the Jaguar 4.1 (Schrodinger, Inc., Portland Oregon) computer code. The energy of each state is computed at the minimum-energy geometry for that state. The difference in energy between the two states is further modified by Equation 1 to give the triplet state energy (E(t)):

$$E(t) = 0.84*(E(ts)-E(gs))+0.35$$

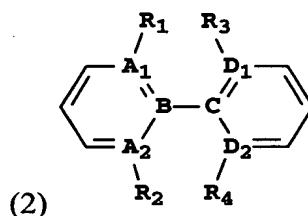
For polymeric or oligomeric materials, it is sufficient to compute the triplet energy over a monomer or oligomer of sufficient size so that additional units do not substantially change the computed triplet energy.

Many benzidine compounds have triplet energies that are too low to make useful hosts for blue and green phosphorescent dopants. For example, when R<sub>1</sub>-R<sub>4</sub> and R<sub>9</sub>-R<sub>12</sub> are hydrogen and R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> are phenyl, the compound shown in Formula (1) has a measured triplet energy of 2.53 eV. This energy is too low to make a useful host for most blue and green phosphorescent dopants, which typically have triplet energy levels in the range of 2.50 to 3.00 eV.

A computational study of the triplet energy of benzidine molecules of Formula (1) wherein R<sub>1</sub>-R<sub>4</sub> and R<sub>9</sub>-R<sub>12</sub> are hydrogen, indicates that the two phenyl groups of the biphenyl linkage become co-planar in the triplet state. However, if the two phenyl groups of the biphenyl linkage are forced to be twisted relative to each other, the energy of the triplet state rises considerably. Such non-co-planarity can be enforced by substitution at least one position corresponding to R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>.

Thus, to obtain a benzidine compound with high triplet energy, it is desirable to choose R<sub>1</sub>-R<sub>4</sub>, of Formula (1), such that the triplet state twist angle of the biphenyl linkage is large. The biphenyl linkage of the benzidine of Formula

(1) can be represented by Formula (2). The triplet state twist angle for the biphenyl linkage in Formula (2) can be calculated using the B3LYP method as implemented in the Gaussian98 (Gaussian, Inc., Pittsburgh, PA) computer program and the basis set defined for triplet state energy. The angle may be  
5 obtained by optimizing the geometry of the lowest triplet state using unrestricted B3LYP. The angle chosen is the maximum of torsions A1-B-C-D1 and A2-B-C-D2.



10 For polymeric materials, it is sufficient to compute the triplet state twist angle of Formula (2) over a monomer or oligomer of sufficient size so that additional polymeric units do not substantially change the twist angle.

The degree of triplet state twist angle required is set by the need for the triplet state energy of the benzidine compound host to be higher than the triplet  
15 state energy of the phosphorescent light-emitting guest material. It is desirable that the triplet state twist angle be at least 20°.

In one useful embodiment of the invention, the substituents R<sub>1</sub>-R<sub>4</sub> are chosen to provide a triplet state twist angle of at least 20°, and the phosphorescent material emits light with a maximum intensity at a wavelength  
20 between 600 and 700 nm.

In another useful embodiment of the invention, the substituents R<sub>1</sub>-R<sub>4</sub> are chosen to provide a triplet state twist angle of at least 20°, and the phosphorescent material emits light with a maximum intensity at a wavelength between 500 and 600 nm.

25 In another useful embodiment of the invention, the substituents R<sub>1</sub>-R<sub>4</sub> are chosen to provide a triplet state twist angle of at least 35°, and the phosphorescent material emits light with a maximum intensity at a wavelength between 400 and 500 nm.



The electroluminescent device incorporating this material may have additional layers chosen from but not limited to the group of: an anode, a cathode, a second light emitting layer, a hole blocking layer, an electron blocking layer, an exciton blocking layer, a hole transport layer, an electron transport layer, a hole injection layer, and an electron injection layer.

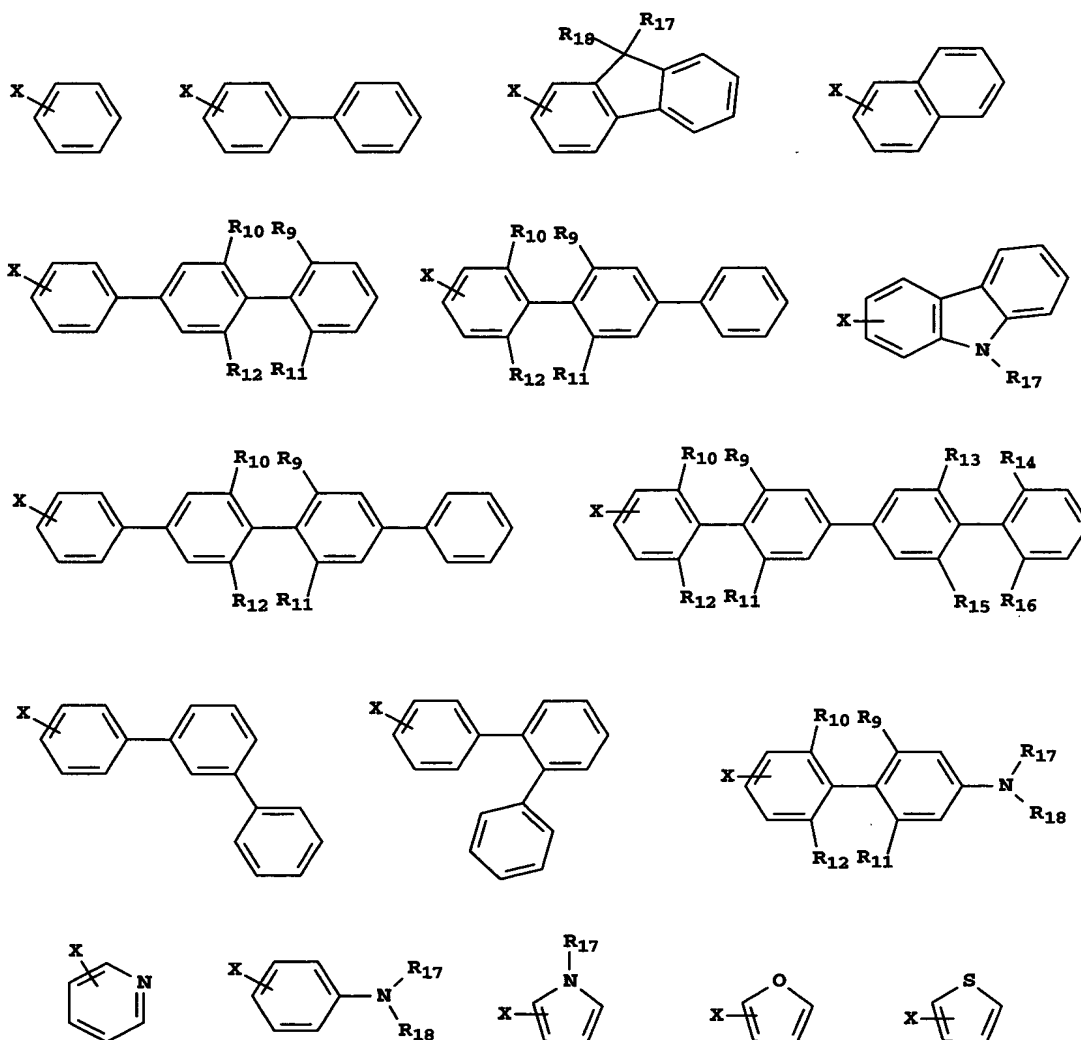
Substituents represented by R<sub>1</sub>-R<sub>4</sub> may be chosen as electron-withdrawing or electron-donating substituents to modify the charge transport and charge trapping properties of the benzidine nucleus.

The Sterimol parameter B<sub>1</sub> may be used to choose substituents R<sub>1</sub>-R<sub>4</sub>. B<sub>1</sub> measures the minimum radius of a substituent perpendicular to the bonding axis and so measures the degree to which the substituent will force the phenyl rings to be non-co-planar. The Sterimol parameters for a substituent group are defined in Hansch and Leo (C. Hansch and A. Leo, *Exploring QSAR Fundamentals and Applications in Chemistry and Biology*, American Chemical Society (1995)). Values for the B<sub>1</sub> Sterimol parameter may be taken from Hansch, Leo and Hoekman (C. Hansch, A. Leo, and D. Hoekman, *Exploring QSAR Hydrophobic, Electronic and Steric Constant*, American Chemical Society (1995)), or if not available in those tables Sterimol parameters can be computed with the commercially available program, TSAR version 3.3 (Accelrys Inc., San Diego, CA). It is desirable that R<sub>1</sub>-R<sub>4</sub> comprise a substituent with a B<sub>1</sub> value of 1.5 or greater. Examples of substituents and their B<sub>1</sub> parameter values are listed in Table A.

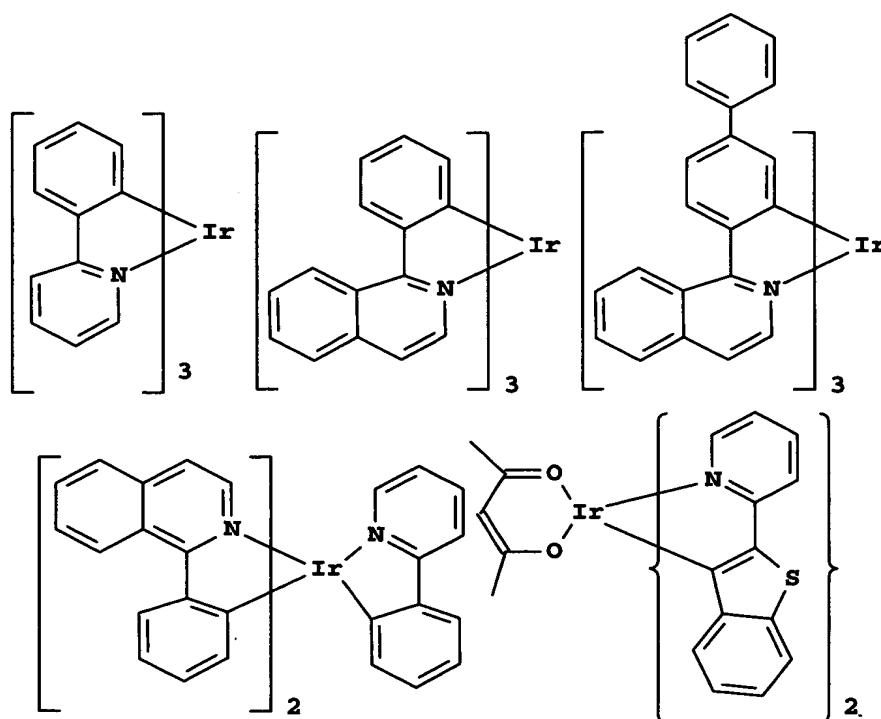
Table A

R <sub>1</sub>	B <sub>1</sub> (angstroms)
CH <sub>3</sub>	1.52
C <sub>2</sub> H <sub>5</sub>	1.52
<i>i</i> -C <sub>4</sub> H <sub>9</sub>	1.52
C <sub>6</sub> H <sub>5</sub>	1.70
<i>c</i> -C <sub>6</sub> H <sub>11</sub>	2.04
CH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	2.11
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	2.59
<i>s</i> -C <sub>4</sub> H <sub>9</sub>	2.59
C(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3.10

It is desirable that R<sub>5</sub>-R<sub>8</sub> be chosen so that the triplet energy of the benzidine nucleus is higher than the triplet energy of the dopant. In one useful embodiment of the invention, R<sub>5</sub>-R<sub>8</sub> represent phenyl groups. In another useful  
5 embodiment of the invention, R<sub>5</sub>-R<sub>8</sub> represent *p*-biphenyl groups. Illustrative examples of possible R<sub>5</sub>-R<sub>8</sub> groups are listed below, wherein R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub> are selected so that the triplet energy of the compound is higher than the triplet energy of the emitting material and may be hydrogen or a substituent group. R<sub>17</sub> and R<sub>18</sub> comprise independently selected substituent  
10 groups. X denotes the ring of the R<sub>5</sub>-R<sub>8</sub> substituent that is attached to the nitrogen of benzidine compound of Formula (1). The substituent groups may be further substituted.



It is desirable that the benzidine host compound be in the same layer as a phosphorescent material. In one useful embodiment of the invention, the phosphorescent material comprises an organometallic complex wherein the metal is selected from the group consisting of Mo, W, Ir, Rh, Os, Pt, and Pd. In one desirable embodiment the organometallic complex comprises a metal that is Ir and at least one ligand that comprises a phenylpyridine group. Illustrative examples of phosphorescent materials are given below.



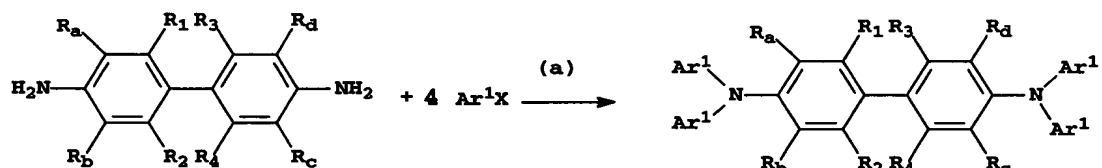
In one useful embodiment of the invention, the benzidine host and  
 5 the phosphorescent material are separate compounds. In another useful  
 embodiment, the benzidine host and the phosphorescent material are part of the  
 same chemical structure such as a copolymer.

### Synthetic Method

10 Benzidine compounds of the invention can be made by various  
 methods described in the literature. For example, reaction of a  
 4,4'-diaminobiphenyl with four equivalents of an aromatic halide under palladium  
 amination conditions can afford the desired benzidine compound (Rxn-1, wherein  
 R<sub>1</sub>-R<sub>4</sub> and R<sub>a</sub>-R<sub>d</sub>, are defined previously and Ar<sup>1</sup> is an aromatic group, X is  
 15 preferably Br or I). Alternatively, the 4,4'-diaminebiphenyl can be reacted with  
 two equivalents of an aromatic halide, resulting in addition of two aromatic  
 groups. This material can be purified and reacted further with one equivalent of  
 second aromatic amine having a different structure. This procedure can be  
 repeated with a third aromatic amine to afford the corresponding benzidine

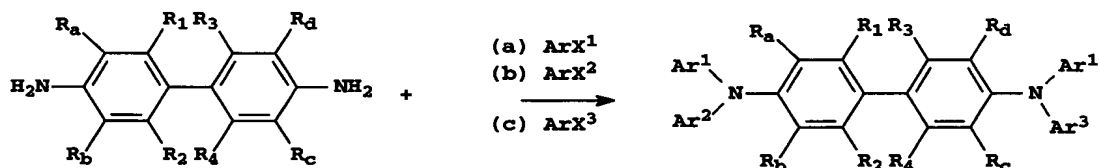
compound (Rxn-2). For examples of palladium amination reactions see J. Hartwig, M. Kawatsura, S. Hauck, K. Shaughnessy, L Alcazar-Roman, *J. Org. Chem.*, **64**, 5575(1999), B. Yang, and S. Buchwald, *J. Organometallic Chem.*, **576** 125 (1999).

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a)  $\text{Pd}(\text{OAc})_2, (t\text{-butyl})_3\text{P}$

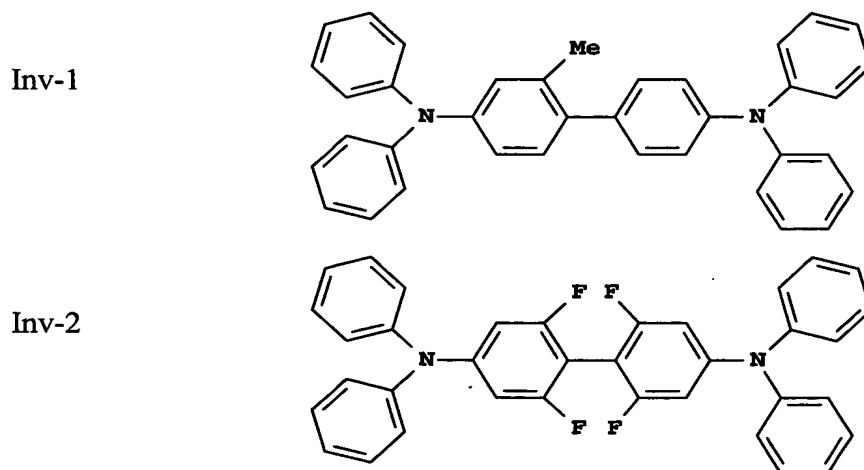
Rxn-1



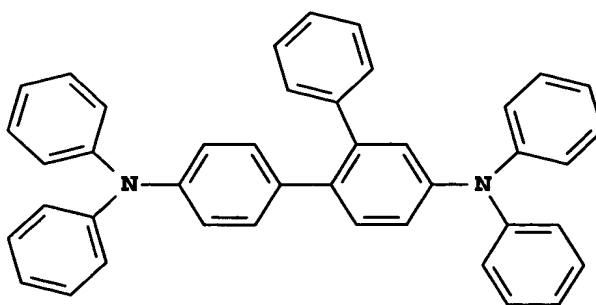
$\text{Pd}(\text{OAc})_2, (t\text{-butyl})_3\text{P}$  is used in each step

10 Rxn-2

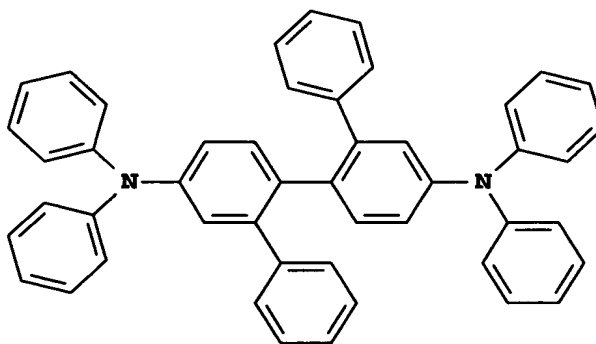
Illustrative examples of substituted benzidine compounds useful in the present invention are the following:



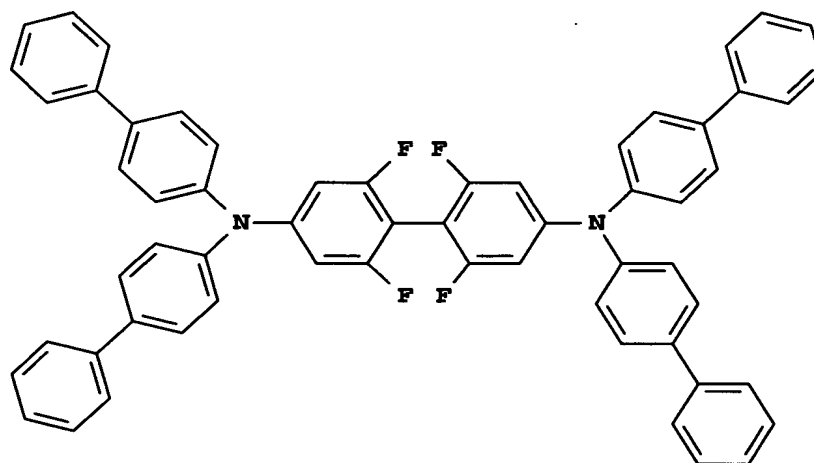
Inv-3



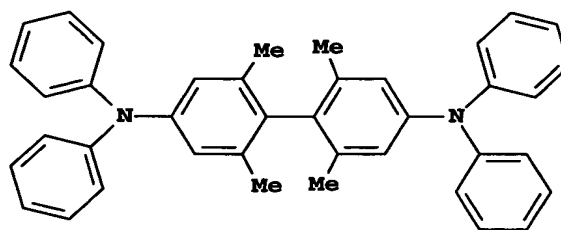
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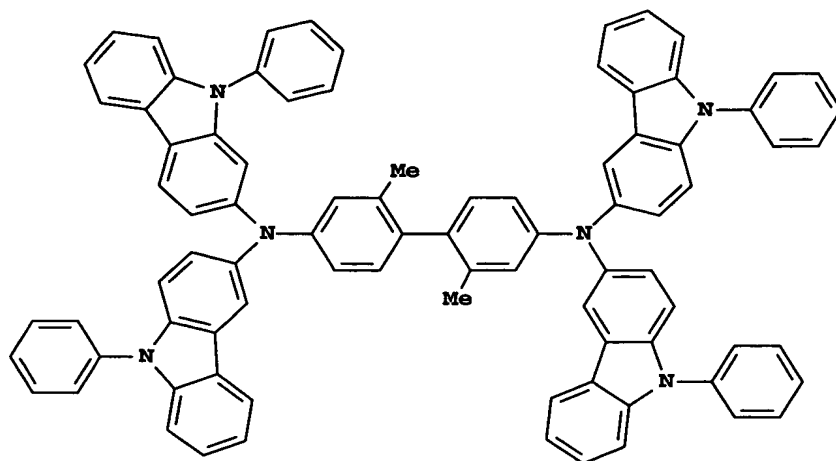
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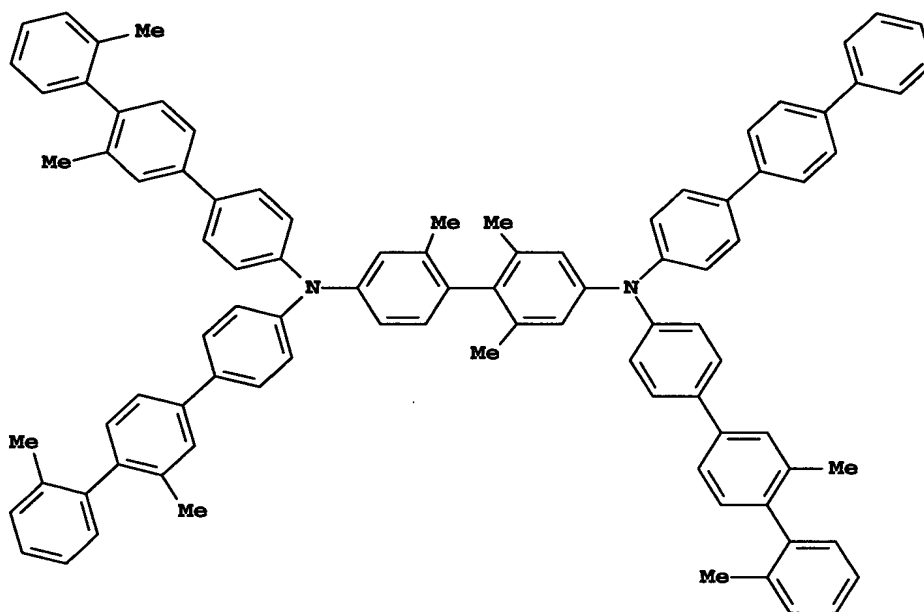
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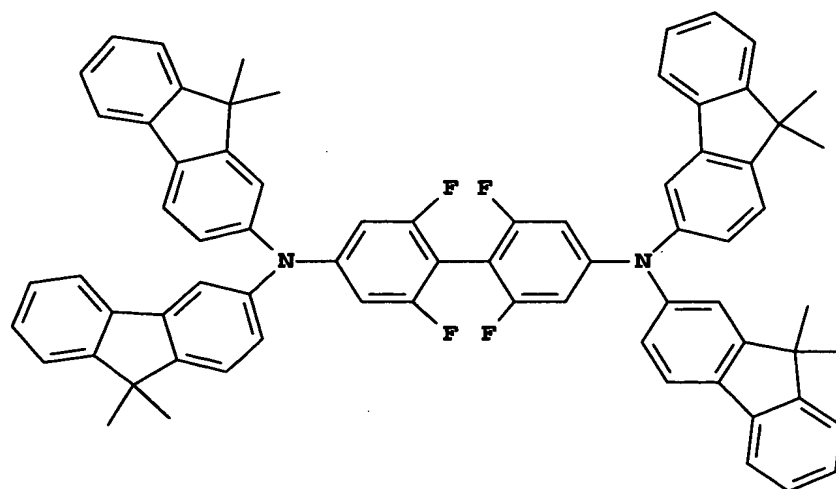
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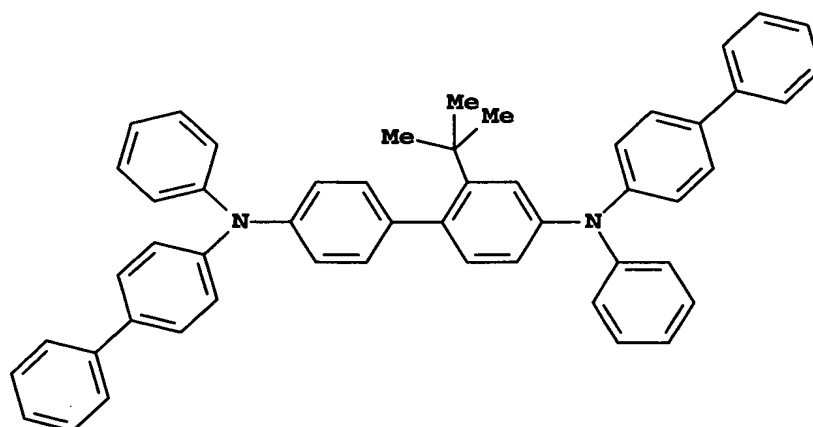
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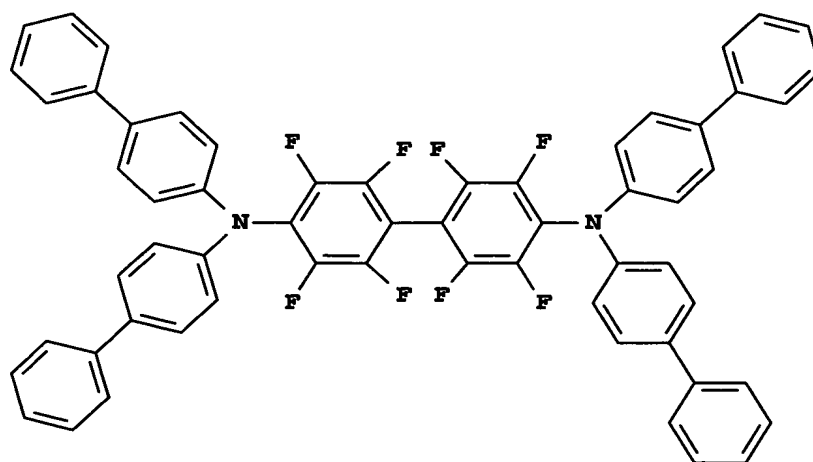
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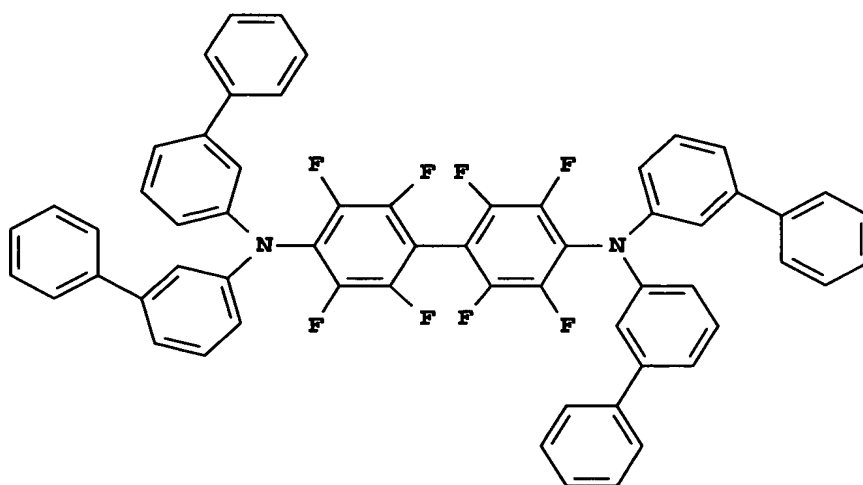
Inv-10



Inv-11

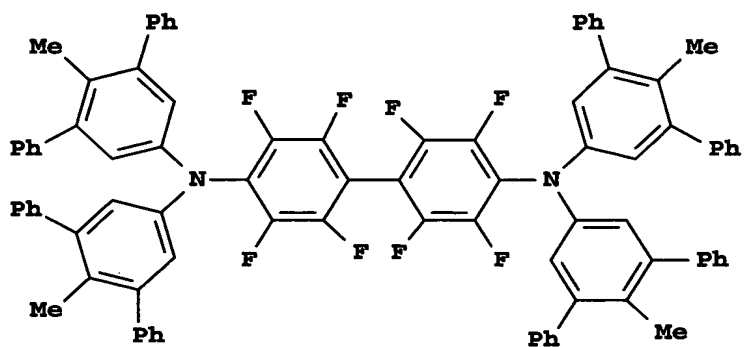


Inv-12

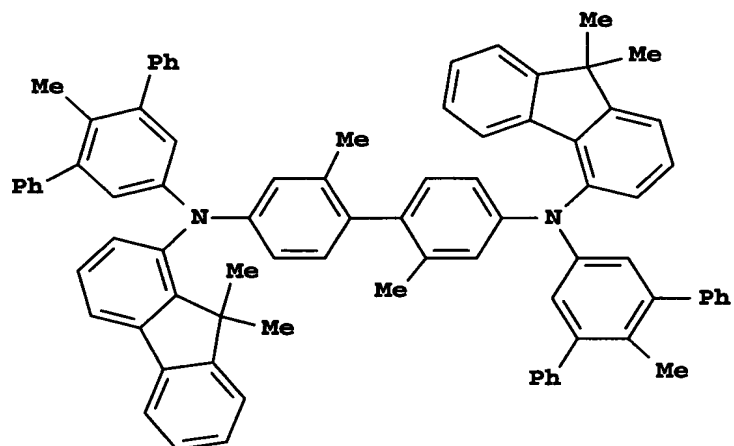




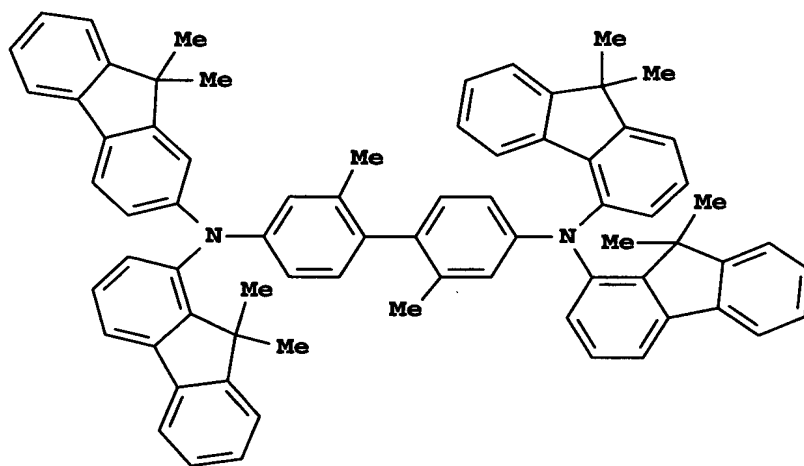
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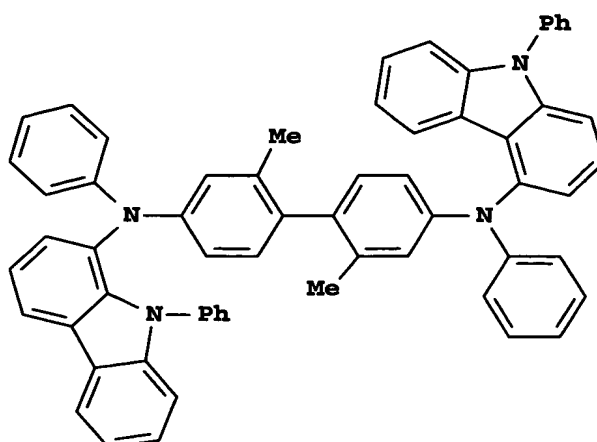
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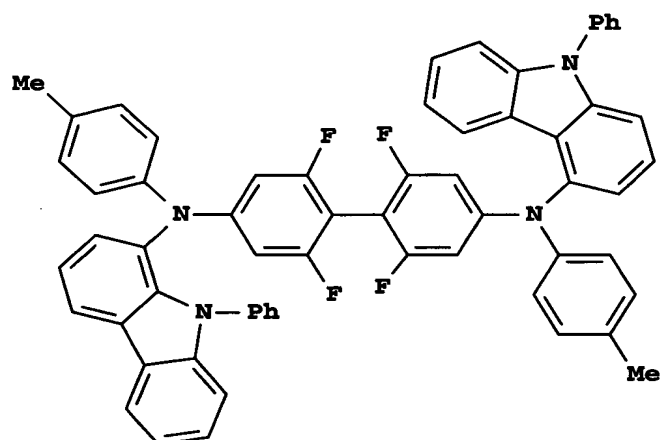
Inv-15



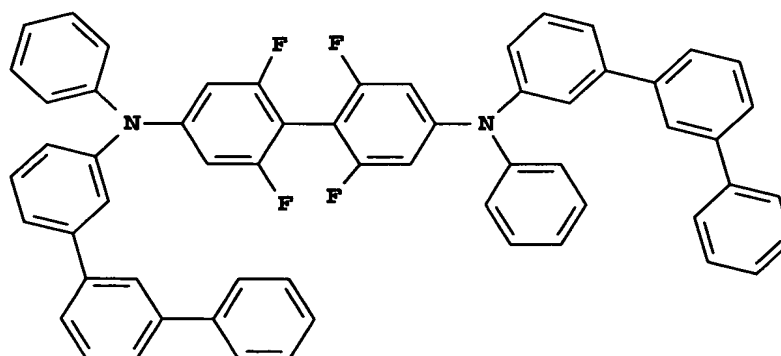
Inv-16



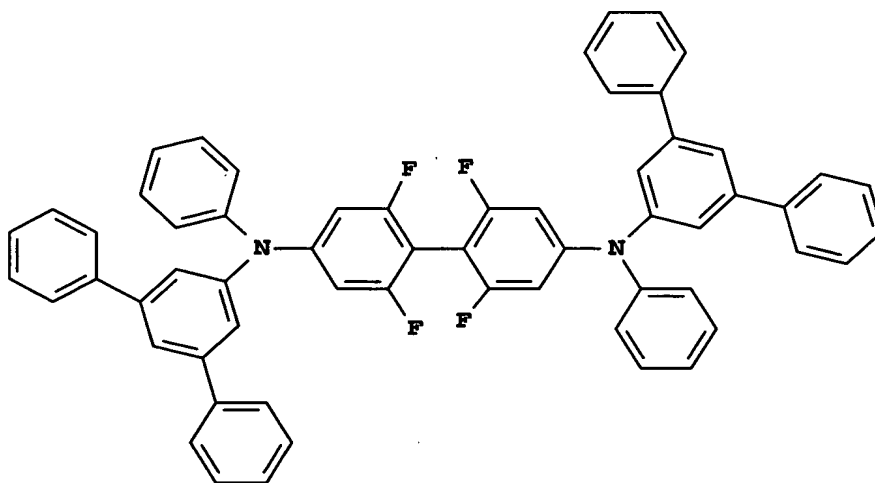
Inv-17



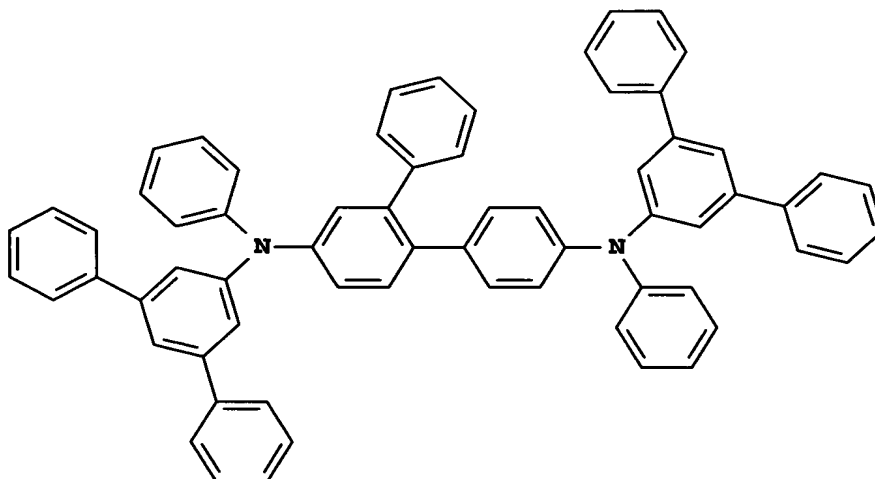
Inv-18



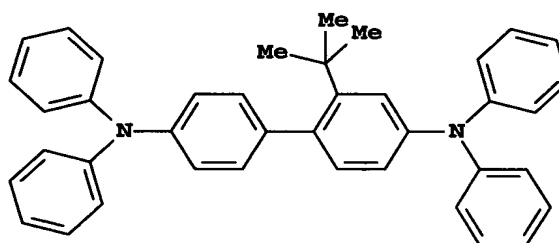
Inv-19



Inv-20



Inv-21



Unless otherwise specifically stated, use of the term "substituted" or "substituent" means any group or atom other than hydrogen. Unless otherwise provided, when a group (including a compound or complex) containing a substitutable hydrogen is referred to, it is also intended to encompass not only the unsubstituted form, but also form further substituted derivatives with any substituent group or groups as herein mentioned, so long as the substituent does

not destroy properties necessary for utility. Suitably, a substituent group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, sulfur, selenium, or boron. The substituent may be, for example, halogen, such as chloro, bromo or fluoro; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain or cyclic alkyl, such as methyl, trifluoromethyl, ethyl, t-butyl, 3-(2,4-di-t-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, sec-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-t-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-t-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-t-pentylphenoxy)acetamido, alpha-(2,4-di-t-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-t-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-t-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-t-pentylphenyl)carbonylamino, p-dodecylphenylcarbonylamino, p-tolylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioctyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-p-tolylureido, N-(m-hexadecylphenyl)ureido, N,N-(2,5-di-t-pentylphenyl)-N'-ethylureido, and t-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, p-tolylsulfonamido, p-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropylsulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl, N-[3-

(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-t-amylphenoxy)acetyl, phenoxycarbonyl, p-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-t-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and p-tolylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and p-tolylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-t-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-t-octylphenylthio, and p-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, p-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbamoyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1 (N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen, sulfur, phosphorous, or boron. such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyloxy; quaternary ammonium, such as triethylammonium; quaternary phosphonium, such as triphenylphosphonium; and silyloxy, such as trimethylsilyloxy.

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired desirable properties for a specific application and can include, for example,  
5 electron-withdrawing groups, electron-donating groups, and steric groups. When a molecule may have two or more substituents, the substituents may be joined together to form a ring such as a fused ring unless otherwise provided. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon  
10 atoms, but greater numbers are possible depending on the particular substituents selected.

Suitably, the light-emitting layer of the OLED device comprises a host material and one or more guest materials for emitting light. At least one of the guest materials is suitably a phosphorescent complex. The light-emitting guest  
15 material(s) is usually present in an amount less than the amount of host materials and is typically present in an amount of up to 15 wt % of the host, more typically from 0.1-5.0 wt % of the host, and commonly 2.0 – 8.0 wt% of the host. For convenience, the phosphorescent complex guest material may be referred to herein as a phosphorescent material. The phosphorescent material is preferably a low  
20 molecular weight compound, but it may also be incorporated into an oligomer or a polymer. It may be provided as a discrete material dispersed in the host material, or it may be bonded in some way to the host material, for example, covalently bonded into a polymeric host.

#### 25 Other Host Materials for Phosphorescent Materials

The host material of the invention may be used alone or in combination with other host materials. Other suitable host materials should be selected so that the triplet exciton can be transferred efficiently from the host material to the phosphorescent material. For this transfer to occur, it is a highly  
30 desirable condition that the excited state energy of the phosphorescent material be lower than the difference in energy between the lowest triplet state and the ground

state of the host. However, the band gap of the host should not be chosen so large as to cause an unacceptable increase in the drive voltage of the OLED. Host materials are described in WO 00/70655 A2; 01/39234 A2; 01/ 93642 A1; 02/074015 A2; 02/15645 A1, and US 20020117662. Suitable hosts include certain  
5 aryl amines, triazoles, indoles and carbazole compounds. Examples of desirable hosts are 4,4'-N,N'-dicarbazole-biphenyl (CBP), 2,2'-dimethyl-4,4'-N,N'-dicarbazole-biphenyl, *m*-(N,N'-dicarbazole)benzene, and poly(N-vinylcarbazole), including their derivatives.

Desirable host materials are capable of forming a continuous film.

10 The light-emitting layer may contain more than one host material in order to improve the device's film morphology, electrical properties, light emission efficiency, and lifetime. The light emitting layer may contain a first host material that has good hole-transporting properties, and a second host material that has good electron-transporting properties.

#### 15 Phosphorescent Materials

Phosphorescent materials may be used alone or in combination with each other, either in the same or different layers. Examples of phosphorescent and related materials are described in WO 00/57676, WO  
20 00/70655, WO 01/41512 A1, WO 02/15645 A1, US 2003/0017361 A1, WO 01/93642 A1, WO 01/39234 A2, US 6,458,475 B1, WO 02/071813 A1, US 6,573,651 B2, US 2002/0197511 A1, WO 02/074015 A2, US 6,451,455 B1, US 2003/ 0072964 A1, US 2003 / 0068528 A1, US 6,413,656 B1, US 6,515,298 B2, US 6,451,415 B1, US 6,097,147, US 2003/0124381 A1, US 2003/0059646 A1,  
25 US 2003/0054198 A1, EP 1 239 526 A2, EP 1 238 981 A2, EP 1 244 155 A2, US 2002/0100906 A1, US 2003 / 0068526 A1, US 2003/0068535 A1, JP 2003073387A, JP 2003 073388A, US 2003/0141809 A1, US 2003/0040627 A1, JP 2003059667A, JP 2003073665A, and US 2002/0121638 A1.

The emission wavelengths of cyclometallated Ir(III) complexes of  
30 the type IrL<sub>3</sub> and IrL<sub>2</sub>L', such as the green-emitting *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)Iridium(III) and bis(2-phenylpyridinato-N,C<sup>2'</sup>)Iridium(III)(acetylacetonate)

may be shifted by substitution of electron donating or withdrawing groups at appropriate positions on the cyclometallating ligand L, or by choice of different heterocycles for the cyclometallating ligand L. The emission wavelengths may also be shifted by choice of the ancillary ligand L'. Examples of red emitters are the bis(2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>)Iridium(III)(acetylacetonate) and tris(1-phenylisoquinolino-N,C)Iridium(III). A blue-emitting example is bis(2-(4,6-difluorophenyl)-pyridinato-N,C<sup>2'</sup>)Iridium(III)(picolate).

Red electrophosphorescence has been reported, using bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-N, C<sup>3'</sup>) iridium (acetylacetonate) [Btp<sub>2</sub>Ir(acac)] as the phosphorescent material (Adachi, C., Lamansky, S., Baldo, M. A., Kwong, R. C., Thompson, M. E., and Forrest, S. R., *App. Phys. Lett.*, **78**, 1622-1624 (2001).

Other important phosphorescent materials include cyclometallated Pt(II) complexes such as cis-bis(2-phenylpyridinato-N,C<sup>2'</sup>)platinum(II), cis-bis(2-(2'-thienyl)pyridinato-N,C<sup>3'</sup>) platinum(II), cis-bis(2-(2'-thienyl)quinolino-N,C<sup>5'</sup>) platinum(II), or (2-(4,6-difluorophenyl)pyridinato-NC<sup>2'</sup>) platinum (II) acetylacetonate. Pt(II) porphyrin complexes such as 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum(II) are also useful phosphorescent materials.

Still other examples of useful phosphorescent materials include coordination complexes of the trivalent lanthanides such as Tb<sup>3+</sup> and Eu<sup>3+</sup> (J. Kido et al, *Appl. Phys. Lett.*, **65**, 2124 (1994))

### Blocking Layers

In addition to suitable hosts, an OLED device employing a phosphorescent material often requires at least one exciton, or hole or electron blocking layers to help confine the excitons or electron-hole recombination centers to the light-emitting layer comprising the host and phosphorescent material. In one embodiment, such a blocking layer would be placed between the electron-transporting layer and the light-emitting layer – see Fig 1, layer 110. In this case, the ionization potential of the blocking layer should be such that there is an energy barrier for hole migration from the host into the electron-transporting layer, while the electron affinity should be such that electrons pass more readily from the



electron-transporting layer into the light-emitting layer comprising host and phosphorescent material. It is further desired, but not absolutely required, that the triplet energy of the blocking material be greater than that of the phosphorescent material. Suitable hole-blocking materials are described in WO 00/70655A2 and  
5 WO 01/93642 A1. Two examples of useful materials are bathocuproine (BCP) and bis(2-methyl-8-quinolinolato)(4-phenylphenolato)Aluminum(III) (BALQ). Metal complexes other than Balq are also known to block holes and excitons as described in US 20030068528. US 20030175553 A1 describes the use of fac-  
tris(1-phenylpyrazolato-N,C 2)iridium(III) (Irppz) in an electron/exciton blocking  
10 layer.

Embodiments of the invention can provide advantageous features such as operating efficiency, higher luminance, color hue, low drive voltage, and improved operating stability. Embodiments of the organometallic compounds useful in the invention can provide a wide range of hues including those useful in  
15 the emission of white light (directly or through filters to provide multicolor displays).

#### General Device Architecture

The present invention can be employed in many OLED device configurations using small molecule materials, oligomeric materials, polymeric  
20 materials, or combinations thereof. These include very simple structures comprising a single anode and cathode to more complex devices, such as passive matrix displays comprised of orthogonal arrays of anodes and cathodes to form pixels, and active-matrix displays where each pixel is controlled independently, for example, with thin film transistors (TFTs).

25 There are numerous configurations of the organic layers wherein the present invention can be successfully practiced. The essential requirements of an OLED are an anode, a cathode, and an organic light-emitting layer located between the anode and cathode. Additional layers may be employed as more fully described hereafter.

A typical structure, especially useful for of a small molecule device, is shown in FIG. 1 and is comprised of a substrate **101**, an anode **103**, a hole-injecting layer **105**, a hole-transporting layer **107**, a light-emitting layer **109**, a hole- or exciton-blocking layer **110**, an electron-transporting layer **111**, and a cathode **113**. These layers are described in detail below. Note that the substrate may alternatively be located adjacent to the cathode, or the substrate may actually constitute the anode or cathode. The organic layers between the anode and cathode are conveniently referred to as the organic EL element. Also, the total combined thickness of the organic layers is desirably less than 500 nm.

The anode and cathode of the OLED are connected to a voltage/current source through electrical conductors. The OLED is operated by applying a potential between the anode and cathode such that the anode is at a more positive potential than the cathode. Holes are injected into the organic EL element from the anode and electrons are injected into the organic EL element at the cathode. Enhanced device stability can sometimes be achieved when the OLED is operated in an AC mode where, for some time period in the cycle, the potential bias is reversed and no current flows. An example of an AC driven OLED is described in US 5,552,678.

#### Substrate

The OLED device of this invention is typically provided over a supporting substrate **101** where either the cathode or anode can be in contact with the substrate. The electrode in contact with the substrate is conveniently referred to as the bottom electrode. Conventionally, the bottom electrode is the anode, but this invention is not limited to that configuration. The substrate can either be light transmissive or opaque, depending on the intended direction of light emission. The light transmissive property is desirable for viewing the EL emission through the substrate. Transparent glass or plastic is commonly employed in such cases. The substrate can be a complex structure comprising multiple layers of materials. This is typically the case for active matrix substrates wherein TFTs are provided below the OLED layers. It is still necessary that the substrate, at least in the emissive pixilated areas, be comprised of largely transparent materials such as glass or

polymers. For applications where the EL emission is viewed through the top electrode, the transmissive characteristic of the bottom support is immaterial, and therefore can be light transmissive, light absorbing or light reflective. Substrates for use in this case include, but are not limited to, glass, plastic, semiconductor materials, silicon, ceramics, and circuit board materials. Again, the substrate can be a complex structure comprising multiple layers of materials such as found in active matrix TFT designs. It is necessary to provide in these device configurations a light-transparent top electrode.

#### Anode

When the desired electroluminescent light emission (EL) is viewed through the anode, the anode should be transparent or substantially transparent to the emission of interest. Common transparent anode materials used in this invention are indium-tin oxide (ITO), indium-zinc oxide (IZO) and tin oxide, but other metal oxides can work including, but not limited to, aluminum- or indium-doped zinc oxide, magnesium-indium oxide, and nickel-tungsten oxide. In addition to these oxides, metal nitrides, such as gallium nitride, and metal selenides, such as zinc selenide, and metal sulfides, such as zinc sulfide, can be used as the anode. For applications where EL emission is viewed only through the cathode, the transmissive characteristics of the anode are immaterial and any conductive material can be used, transparent, opaque or reflective. Example conductors for this application include, but are not limited to, gold, iridium, molybdenum, palladium, and platinum. Typical anode materials, transmissive or otherwise, have a work function of 4.1 eV or greater. Desired anode materials are commonly deposited by any suitable means such as evaporation, sputtering, chemical vapor deposition, or electrochemical means. Anodes can be patterned using well-known photolithographic processes. Optionally, anodes may be polished prior to application of other layers to reduce surface roughness so as to minimize shorts or enhance reflectivity.

#### Cathode

When light emission is viewed solely through the anode, the cathode used in this invention can be comprised of nearly any conductive material.

Desirable materials have good film-forming properties to ensure good contact with the underlying organic layer, promote electron injection at low voltage, and have good stability. Useful cathode materials often contain a low work function metal ( $< 4.0$  eV) or metal alloy. One useful cathode material is comprised of a Mg:Ag alloy wherein the percentage of silver is in the range of 1 to 20 %, as described in U.S. Patent No. 4,885,221. Another suitable class of cathode materials includes bilayers comprising the cathode and a thin electron-injection layer (EIL) in contact with an organic layer (e.g., an electron transporting layer (ETL)) which is capped with a thicker layer of a conductive metal. Here, the EIL preferably includes a low work function metal or metal salt, and if so, the thicker capping layer does not need to have a low work function. One such cathode is comprised of a thin layer of LiF followed by a thicker layer of Al as described in U.S. Patent No. 5,677,572. An ETL material doped with an alkali metal, for example, Li-doped Alq, is another example of a useful EIL. Other useful cathode material sets include, but are not limited to, those disclosed in U.S. Patent Nos. 5,059,861, 5,059,862, and 6,140,763.

When light emission is viewed through the cathode, the cathode must be transparent or nearly transparent. For such applications, metals must be thin or one must use transparent conductive oxides, or a combination of these materials. Optically transparent cathodes have been described in more detail in US 4,885,211, US 5,247,190, JP 3,234,963, US 5,703,436, US 5,608,287, US 5,837,391, US 5,677,572, US 5,776,622, US 5,776,623, US 5,714,838, US 5,969,474, US 5,739,545, US 5,981,306, US 6,137,223, US 6,140,763, US 6,172,459, EP 1 076 368, US 6,278,236, and US 6,284,3936. Cathode materials are typically deposited by any suitable method such as evaporation, sputtering, or chemical vapor deposition. When needed, patterning can be achieved through many well known methods including, but not limited to, through-mask deposition, integral shadow masking as described in US 5,276,380 and EP 0 732 868, laser ablation, and selective chemical vapor deposition.

Hole-Injecting Layer (HIL)

A hole-injecting layer **105** may be provided between anode **103** and hole-transporting layer **107**. The hole-injecting material can serve to improve the film formation property of subsequent organic layers and to facilitate injection of holes into the hole-transporting layer. Suitable materials for use in the hole-injecting layer include, but are not limited to, porphyrinic compounds as described in US 4,720,432, plasma-deposited fluorocarbon polymers as described in US 6,208,075, and some aromatic amines, for example, m-MTDATA (4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine). Alternative hole-injecting materials reportedly useful in organic EL devices are described in EP 0 891 121 A1 and EP 1 029 909 A1.

Hole-Transporting Layer (HTL)

The hole-transporting layer **107** of the organic EL device contains at least one hole-transporting compound such as an aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylaminines are illustrated by Klupfel et al. US 3,180,730. Other suitable triarylaminines substituted with one or more vinyl radicals and/or comprising at least one active hydrogen containing group are disclosed by Brantley et al US 3,567,450 and US 3,658,520.

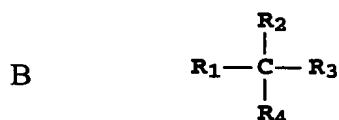
A more preferred class of aromatic tertiary amines are those which include at least two aromatic tertiary amine moieties as described in US 4,720,432 and US 5,061,569. Such compounds include those represented by structural formula (A).



wherein Q<sub>1</sub> and Q<sub>2</sub> are independently selected aromatic tertiary amine moieties and G is a linking group such as an arylene, cycloalkylene, or alkylene group of a

carbon to carbon bond. In one embodiment, at least one of Q<sub>1</sub> or Q<sub>2</sub> contains a polycyclic fused ring structure, e.g., a naphthalene. When G is an aryl group, it is conveniently a phenylene, biphenylene, or naphthalene moiety.

A useful class of triarylamines satisfying structural formula (A) and  
5 containing two triarylamine moieties is represented by structural formula (B):



where

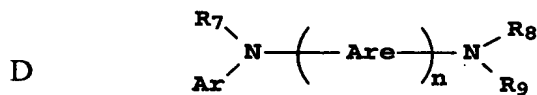
R<sub>1</sub> and R<sub>2</sub> each independently represents a hydrogen atom, an aryl group, or an alkyl group or R<sub>1</sub> and R<sub>2</sub> together represent the atoms completing a cycloalkyl group; and

10 R<sub>3</sub> and R<sub>4</sub> each independently represents an aryl group, which is in turn substituted with a diaryl substituted amino group, as indicated by structural formula (C):



wherein R<sub>5</sub> and R<sub>6</sub> are independently selected aryl groups. In one embodiment, at least one of R<sub>5</sub> or R<sub>6</sub> contains a polycyclic fused ring structure, e.g., a naphthalene.

15 Another class of aromatic tertiary amines are the tetraaryldiamines. Desirable tetraaryldiamines include two diarylamino groups, such as indicated by formula (C), linked through an arylene group. Useful tetraaryldiamines include those represented by formula (D).



wherein

20 each Are is an independently selected arylene group, such as a phenylene or anthracene moiety,

n is an integer of from 1 to 4, and

Ar, R<sub>7</sub>, R<sub>8</sub>, and R<sub>9</sub> are independently selected aryl groups.

In a typical embodiment, at least one of Ar, R<sub>7</sub>, R<sub>8</sub>, and R<sub>9</sub> is a polycyclic fused ring structure, e.g., a naphthalene

The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (A), (B), (C), (D), can each in turn be substituted.

5 Typical substituents include alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halogen such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 6 carbon atoms. The cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms--e.g., cyclopentyl, cyclohexyl, and cycloheptyl  
10 ring structures. The aryl and arylene moieties are usually phenyl and phenylene moieties.

The hole-transporting layer can be formed of a single or a mixture of aromatic tertiary amine compounds. Specifically, one may employ a triarylamine, such as a triarylamine satisfying the formula (B), in combination  
15 with a tetraaryldiamine, such as indicated by formula (D). When a triarylamine is employed in combination with a tetraaryldiamine, the latter is positioned as a layer interposed between the triarylamine and the electron injecting and transporting layer. Illustrative of useful aromatic tertiary amines are the following:

1,1-Bis(4-di-*p*-tolylaminophenyl)cyclohexane  
20 1,1-Bis(4-di-*p*-tolylaminophenyl)-4-phenylcyclohexane  
N,N,N',N'-tetraphenyl-4,4'''-diamino-1,1':4',1'':4'',1'''-quaterphenyl  
Bis(4-dimethylamino-2-methylphenyl)phenylmethane  
1,4-bis[2-[4-[N,N-di(*p*-tolyl)amino]phenyl]vinyl]benzene (BDTAPVB)  
N,N,N',N'-Tetra-*p*-tolyl-4,4'-diaminobiphenyl  
25 N,N,N',N'-Tetraphenyl-4,4'-diaminobiphenyl  
N,N,N',N'-tetra-1-naphthyl-4,4'-diaminobiphenyl  
N,N,N',N'-tetra-2-naphthyl-4,4'-diaminobiphenyl  
N-Phenylcarbazole  
4,4'-Bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB)  
30 4,4'-Bis[N-(1-naphthyl)-N-(2-naphthyl)amino]biphenyl (TNB)  
4,4'-Bis[N-(1-naphthyl)-N-phenylamino]*p*-terphenyl

4,4'-Bis[N-(2-naphthyl)-N-phenylamino]biphenyl  
4,4'-Bis[N-(3-acenaphthenyl)-N-phenylamino]biphenyl  
1,5-Bis[N-(1-naphthyl)-N-phenylamino]naphthalene  
4,4'-Bis[N-(9-anthryl)-N-phenylamino]biphenyl  
5 4,4'-Bis[N-(1-anthryl)-N-phenylamino]-*p*-terphenyl  
4,4'-Bis[N-(2-phenanthryl)-N-phenylamino]biphenyl  
4,4'-Bis[N-(8-fluoranthryl)-N-phenylamino]biphenyl  
4,4'-Bis[N-(2-pyrenyl)-N-phenylamino]biphenyl  
4,4'-Bis[N-(2-naphthacenyl)-N-phenylamino]biphenyl  
10 4,4'-Bis[N-(2-perylenyl)-N-phenylamino]biphenyl  
4,4'-Bis[N-(1-coronenyl)-N-phenylamino]biphenyl  
2,6-Bis(di-*p*-tolylamino)naphthalene  
2,6-Bis[di-(1-naphthyl)amino]naphthalene  
2,6-Bis[N-(1-naphthyl)-N-(2-naphthyl)amino]naphthalene  
15 N,N,N',N'-Tetra(2-naphthyl)-4,4"-diamino-*p*-terphenyl  
4,4'-Bis{N-phenyl-N-[4-(1-naphthyl)-phenyl]amino}biphenyl  
2,6-Bis[N,N-di(2-naphthyl)amino]fluorene  
4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine (MTDATA)  
4,4'-Bis[N-(3-methylphenyl)-N-phenylamino]biphenyl (TPD)

20 Another class of useful hole-transporting materials includes polycyclic aromatic compounds as described in EP 1 009 041. Tertiary aromatic amines with more than two amine groups may be used including oligomeric materials. In addition, polymeric hole-transporting materials can be used such as poly(N-vinylcarbazole) (PVK), polythiophenes, polypyrrole, polyaniline, and  
25 copolymers such as poly(3,4-ethylenedioxythiophene) / poly(4-styrenesulfonate) also called PEDOT/PSS.

#### Fluorescent Light-Emitting Materials and Layers (LEL)

In addition to the phosphorescent materials of this invention, other light emitting materials may be used in the OLED device, including fluorescent  
30 materials. Although the term "fluorescent" is commonly used to describe any



light emitting material, in this case we are referring to a material that emits light from a singlet excited state. Fluorescent materials may be used in the same layer as the phosphorescent material, in adjacent layers, in adjacent pixels, or any combination. Care must be taken not to select materials that will adversely affect the performance of the phosphorescent materials of this invention. One skilled in the art will understand that triplet excited state energies of materials in the same layer as the phosphorescent material or in an adjacent layer must be appropriately set so as to prevent unwanted quenching.

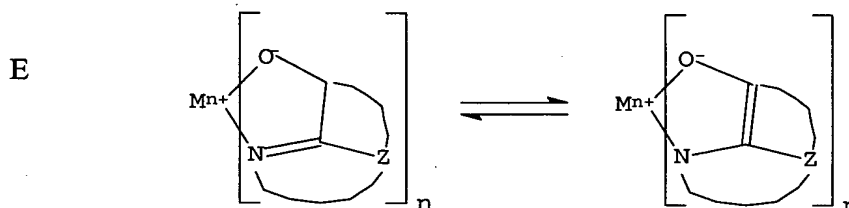
As more fully described in U.S. Patent Nos. 4,769,292 and 5,935,721, the light-emitting layer (LEL) of the organic EL element includes a luminescent fluorescent or phosphorescent material where electroluminescence is produced as a result of electron-hole pair recombination in this region. The light-emitting layer can be comprised of a single material, but more commonly consists of a host material doped with a guest emitting material or materials where light emission comes primarily from the emitting materials and can be of any color. The host materials in the light-emitting layer can be an electron-transporting material, as defined below, a hole-transporting material, as defined above, or another material or combination of materials that support hole-electron recombination. Fluorescent emitting materials are typically incorporated at 0.01 to 10 % by weight of the host material.

The host and emitting materials can be small non-polymeric molecules or polymeric materials such as polyfluorenes and polyvinylarylenes (e.g., poly(p-phenylenevinylene), PPV).. In the case of polymers, small molecule emitting materials can be molecularly dispersed into a polymeric host, or the emitting materials can be added by copolymerizing a minor constituent into a host polymer. Host materials may be mixed together in order to improve film formation, electrical properties, light emission efficiency, lifetime, or manufacturability. The host may comprise a material that has good hole-transporting properties and a material that has good electron-transporting properties.

An important relationship for choosing a fluorescent dye as a guest emitting material is a comparison of the singlet excited state energies of the host and light-emitting material. For efficient energy transfer from the host to the emitting material, a highly desirable condition is that the singlet excited state energy of the emitting material is lower than that of the host material.

Host and emitting materials known to be of use include, but are not limited to, those disclosed in US 4,768,292, US 5,141,671, US 5,150,006, US 5,151,629, US 5,405,709, US 5,484,922, US 5,593,788, US 5,645,948, US 5,683,823, US 5,755,999, US 5,928,802, US 5,935,720, US 5,935,721, and US 6,020,078.

Metal complexes of 8-hydroxyquinoline and similar derivatives (Formula E) constitute one class of useful host compounds capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 500 nm, e.g., green, yellow, orange, and red.



wherein

M represents a metal;

n is an integer of from 1 to 4; and

Z independently in each occurrence represents the atoms completing a nucleus having at least two fused aromatic rings.

From the foregoing it is apparent that the metal can be monovalent, divalent, trivalent, or tetravalent metal. The metal can, for example, be an alkali metal, such as lithium, sodium, or potassium; an alkaline earth metal, such as magnesium or calcium; an earth metal, such aluminum or gallium, or a transition metal such as zinc or zirconium. Generally any monovalent, divalent, trivalent, or tetravalent metal known to be a useful chelating metal can be employed.

Z completes a heterocyclic nucleus containing at least two fused aromatic rings, at least one of which is an azole or azine ring. Additional rings, including both aliphatic and aromatic rings, can be fused with the two required rings, if required. To avoid adding molecular bulk without improving on function the number of ring atoms is usually maintained at 18 or less.

Illustrative of useful chelated oxinoid compounds are the following:

CO-1: Aluminum trisoxine [alias, tris(8-quinolinolato)aluminum(III)]

CO-2: Magnesium bisoxine [alias, bis(8-quinolinolato)magnesium(II)]

10 CO-3: Bis[benzo {f} -8-quinolinolato]zinc (II)

CO-4: Bis(2-methyl-8-quinolinolato)aluminum(III)- $\mu$ -oxo-bis(2-methyl-8-quinolinolato) aluminum(III)

CO-5: Indium trisoxine [alias, tris(8-quinolinolato)indium]

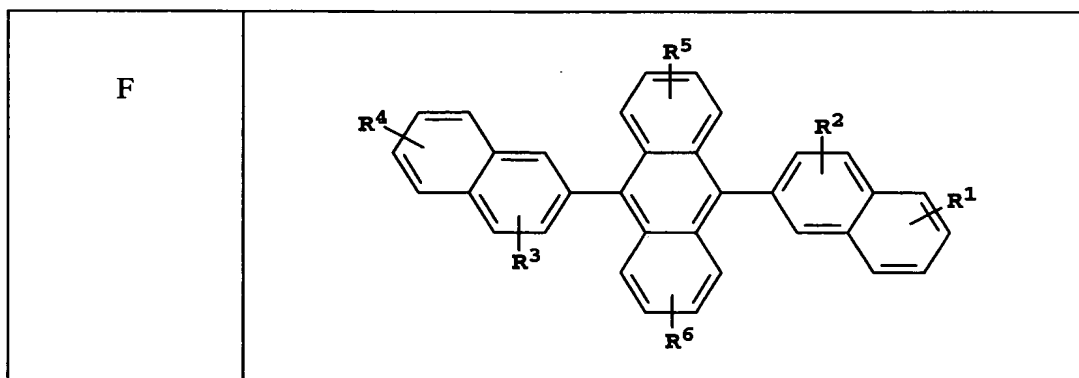
15 CO-6: Aluminum tris(5-methyloxine) [alias, tris(5-methyl-8-quinolinolato) aluminum(III)]

CO-7: Lithium oxine [alias, (8-quinolinolato)lithium(I)]

CO-8: Gallium oxine [alias, tris(8-quinolinolato)gallium(III)]

CO-9: Zirconium oxine [alias, tetra(8-quinolinolato)zirconium(IV)]

20 Derivatives of 9,10-di-(2-naphthyl)anthracene (Formula F) constitute one class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g., blue, green, yellow, orange or red.



wherein:  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  represent one or more substituents on each ring where each substituent is individually selected from the following groups:

Group 1: hydrogen, or alkyl of from 1 to 24 carbon atoms;

Group 2: aryl or substituted aryl of from 5 to 20 carbon atoms;

5      Group 3: carbon atoms from 4 to 24 necessary to complete a fused aromatic ring of anthracenyl; pyrenyl, or perylenyl;

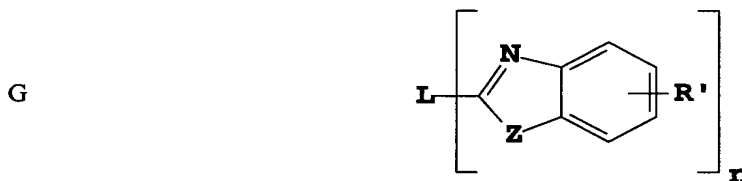
Group 4: heteroaryl or substituted heteroaryl of from 5 to 24 carbon atoms as necessary to complete a fused heteroaromatic ring of furyl, thienyl, pyridyl, quinolinyl or other heterocyclic systems;

10      Group 5: alkoxyamino, alkylamino, or arylamino of from 1 to 24 carbon atoms; and

Group 6: fluorine, chlorine, bromine or cyano.

Illustrative examples include 9,10-di-(2-naphthyl)anthracene and 2-*t*-butyl-9,10-di-(2-naphthyl)anthracene. Other anthracene derivatives can be useful  
15 as a host in the LEL, including derivatives of 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene.

Benzazole derivatives (Formula G) constitute another class of useful host materials capable of supporting electroluminescence, and are particularly suitable for light emission of wavelengths longer than 400 nm, e.g.,  
20 blue, green, yellow, orange or red.



Where:

n is an integer of 3 to 8;

Z is O, NR or S; and

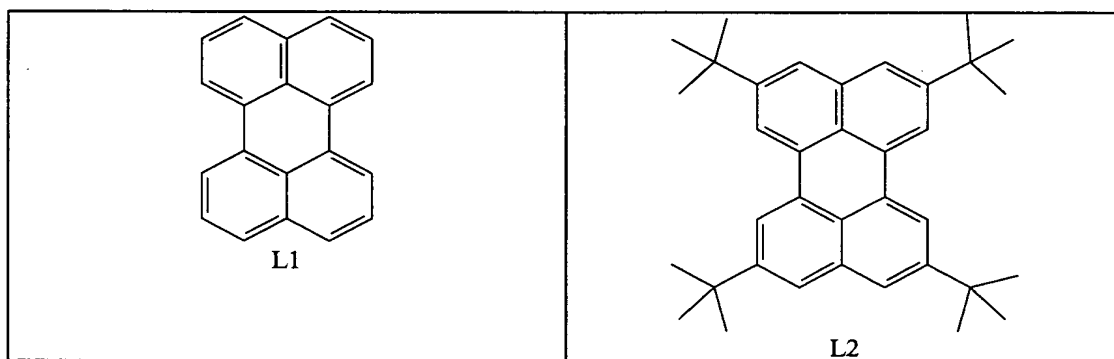
R and R' are individually hydrogen; alkyl of from 1 to 24 carbon atoms,  
25 for example, propyl, *t*-butyl, heptyl, and the like; aryl or hetero-atom substituted aryl of from 5 to 20 carbon atoms for example phenyl and naphthyl, furyl, thienyl,

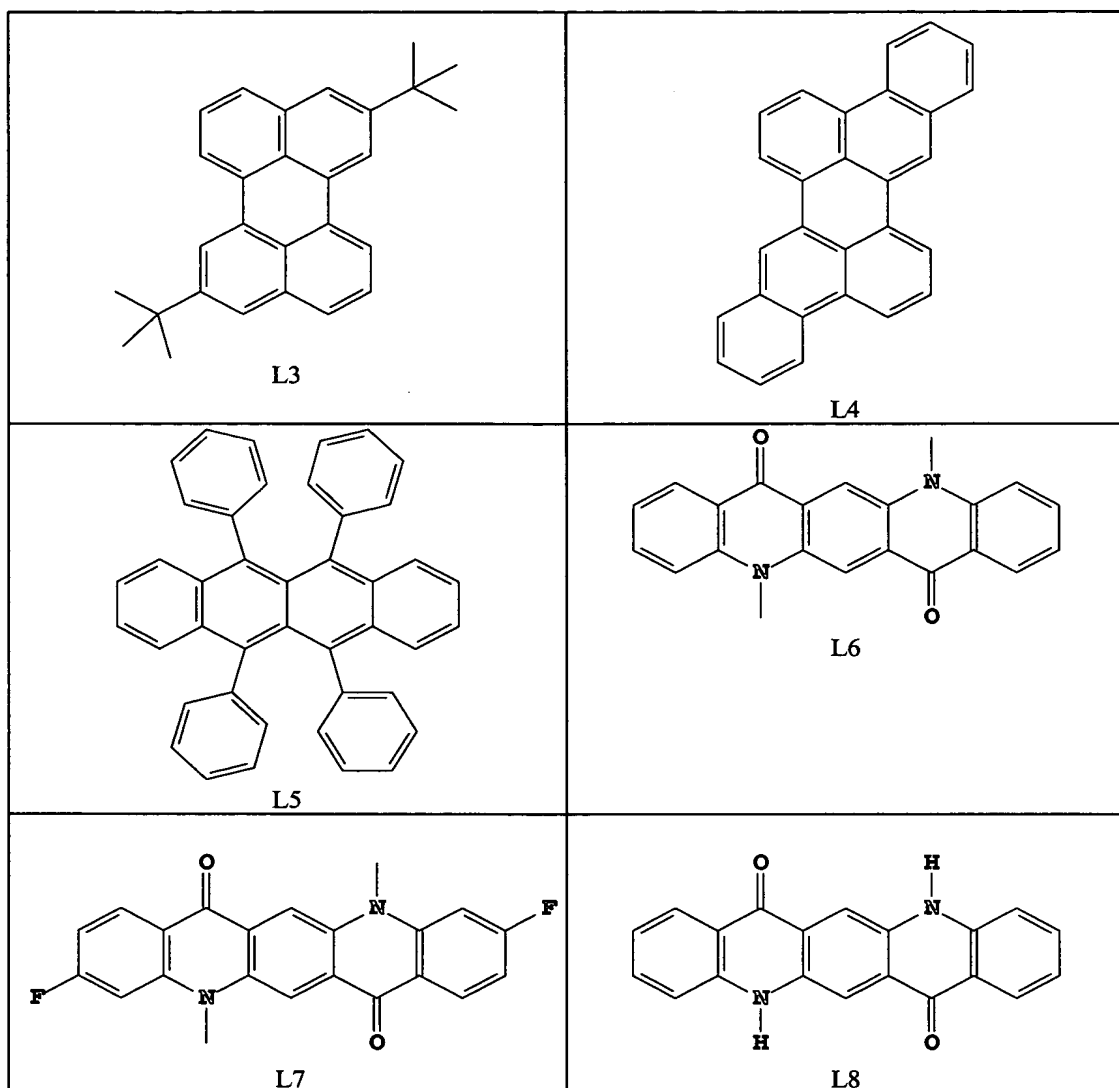
pyridyl, quinolinyl and other heterocyclic systems; or halo such as chloro, fluoro; or atoms necessary to complete a fused aromatic ring; and

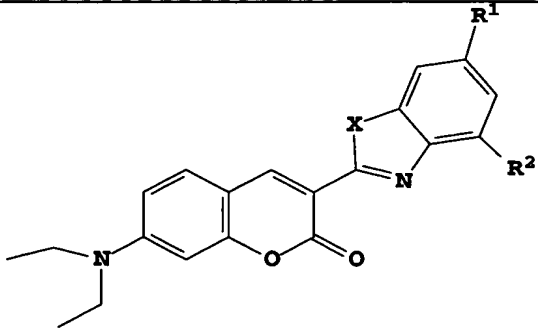
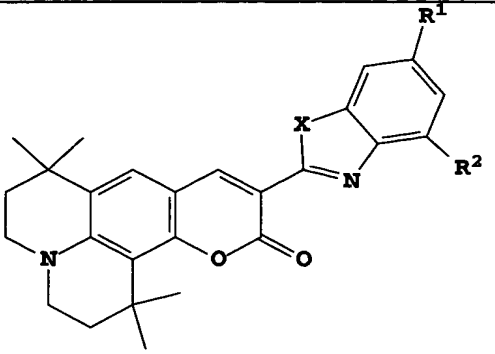
L is a linkage unit consisting of alkyl, aryl, substituted alkyl, or substituted aryl, which conjugately or unconjugately connects the multiple benzazoles  
5 together. An example of a useful benzazole is 2, 2', 2''-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole].

Styrylarylene derivatives as described in U.S. Patent 5,121,029 and JP  
08333569 are also useful hosts for blue emission. For example, 9,10-bis[4-(2,2-  
diphenylethenyl)phenyl]anthracene and 4,4'-Bis(2,2-diphenylethenyl)-1,1'-  
10 biphenyl (DPVBi) are useful hosts for blue emission.

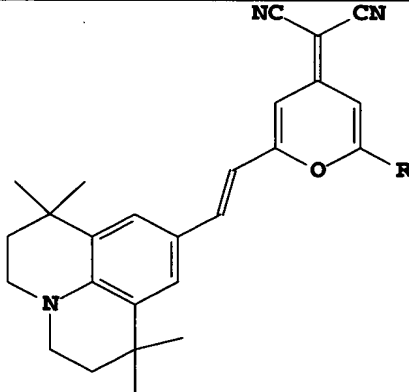
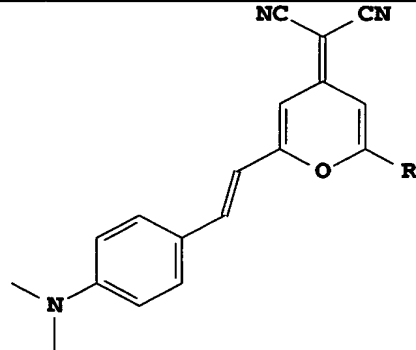
Useful fluorescent emitting materials include, but are not limited  
to, derivatives of anthracene, tetracene, xanthene, perylene, rubrene, coumarin,  
rhodamine, and quinacridone, dicyanomethylenepyran compounds, thiopyran  
15 compounds, polymethine compounds, pyrilium and thiapyrilium compounds,  
fluorene derivatives, perflanthene derivatives, indenoperylene derivatives,  
bis(azinyl)amine boron compounds, bis(azinyl)methane compounds, and  
carbostyryl compounds. Illustrative examples of useful materials include, but are  
not limited to, the following:

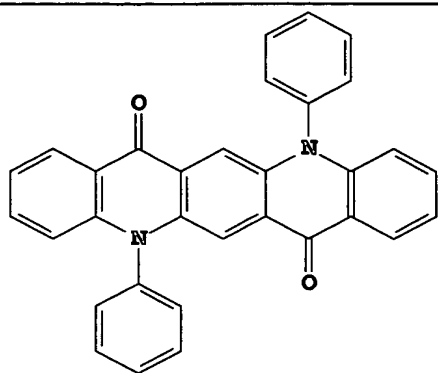




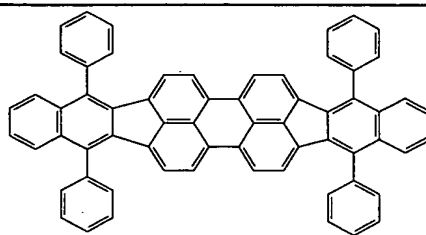
							
	<u>X</u>	<u>R1</u>	<u>R2</u>		<u>X</u>	<u>R1</u>	<u>R2</u>
L9	O	H	H	L23	O	H	H
L10	O	H	Methyl	L24	O	H	Methyl
L11	O	Methyl	H	L25	O	Methyl	H
L12	O	Methyl	Methyl	L26	O	Methyl	Methyl
L13	O	H	t-butyl	L27	O	H	t-butyl
L14	O	t-butyl	H	L28	O	t-butyl	H
L15	O	t-butyl	t-butyl	L29	O	t-butyl	t-butyl
L16	S	H	H	L30	S	H	H
L17	S	H	Methyl	L31	S	H	Methyl
L18	S	Methyl	H	L32	S	Methyl	H
L19	S	Methyl	Methyl	L33	S	Methyl	Methyl
L20	S	H	t-butyl	L34	S	H	t-butyl
L21	S	t-butyl	H	L35	S	t-butyl	H
L22	S	t-butyl	t-butyl	L36	S	t-butyl	t-butyl

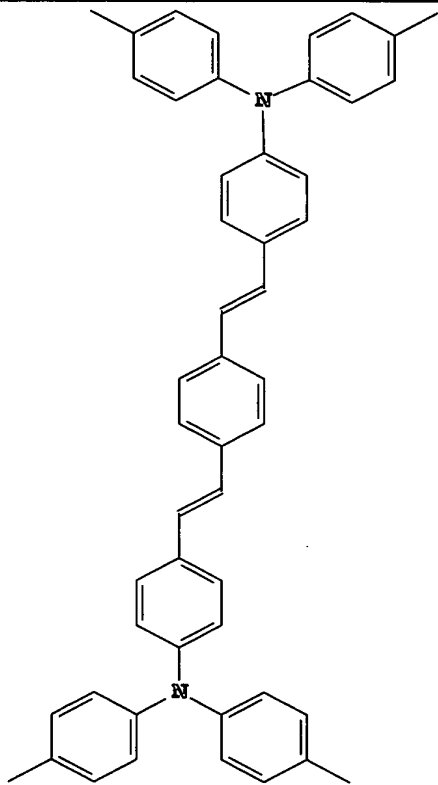
			
	<u>R</u>		<u>R</u>
L37	phenyl	L41	phenyl
L38	methyl	L42	methyl
L39	t-butyl	L43	t-butyl
L40	mesityl	L44	mesityl



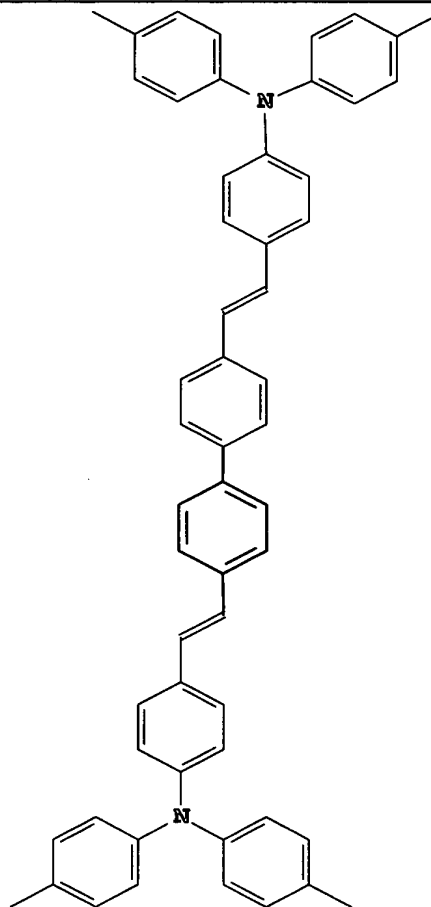
L45



L46

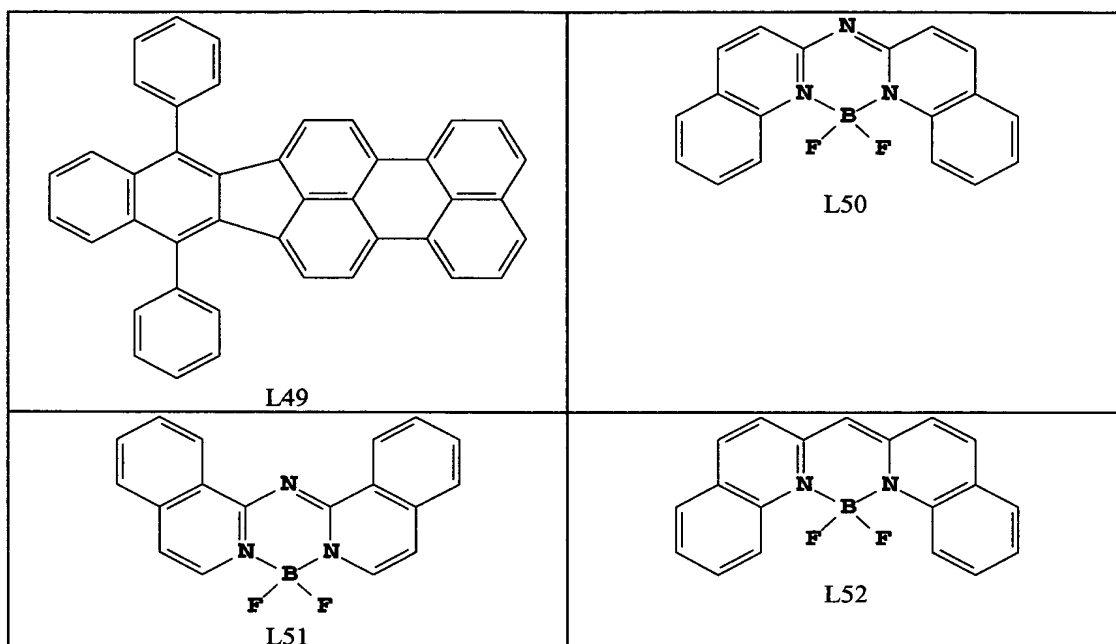


L47



L48





#### Electron-Transporting Layer (ETL)

Preferred thin film-forming materials for use in forming the electron-transporting layer 111 of the organic EL devices of this invention are metal chelated oxinoid compounds, including chelates of oxine itself (also commonly referred to as 8-quinolinol or 8-hydroxyquinoline). Such compounds help to inject and transport electrons and exhibit both high levels of performance and are readily fabricated in the form of thin films. Exemplary of contemplated oxinoid compounds are those satisfying structural formula (E), previously described.

Other electron-transporting materials include various butadiene derivatives as disclosed in US 4,356,429 and various heterocyclic optical brighteners as described in US 4,539,507. Benzazoles satisfying structural formula (G) are also useful electron transporting materials. Triazines are also known to be useful as electron transporting materials.

#### Other Useful Organic Layers and Device Architecture

In some instances, layers 109 through 111 can optionally be collapsed into a single layer that serves the function of supporting both light emission and electron transportation. Layers 110 and 111 may also be collapsed

into a single layer that functions to block holes or excitons, and supports electron transportation. It also known in the art that emitting materials may be included in the hole-transporting layer, which may serve as a host. Multiple materials may be added to one or more layers in order to create a white-emitting OLED, for  
5 example, by combining blue- and yellow-emitting materials, cyan- and red-emitting materials, or red-, green-, and blue-emitting materials. White-emitting devices are described, for example, in EP 1 187 235, US 20020025419, EP 1 182 244, US 5,683,823, US 5,503,910, US 5,405,709, and US 5,283,182 and can be equipped with a suitable filter arrangement to produce a color emission.

10 This invention may be used in so-called stacked device architecture, for example, as taught in US 5,703,436 and US 6,337,492.

#### Deposition of Organic Layers

The organic materials mentioned above are suitably deposited by any means suitable for the form of the organic materials. In the case of small  
15 molecules, they are conveniently deposited through sublimation, but can be deposited by other means such as from a solvent with an optional binder to improve film formation. If the material is a polymer, solvent deposition is usually preferred. The material to be deposited by sublimation can be vaporized from a sublimator "boat" often comprised of a tantalum material, e.g., as described in US  
20 6,237,529, or can be first coated onto a donor sheet and then sublimed in closer proximity to the substrate. Layers with a mixture of materials can utilize separate sublimator boats or the materials can be pre-mixed and coated from a single boat or donor sheet. Patterned deposition can be achieved using shadow masks, integral shadow masks (US 5,294,870), spatially-defined thermal dye transfer from a  
25 donor sheet (US 5,688,551, US 5,851,709 and US 6,066,357) and inkjet method (US 6,066,357).

#### Encapsulation

Most OLED devices are sensitive to moisture or oxygen, or both, so they are commonly sealed in an inert atmosphere such as nitrogen or argon,  
30 along with a desiccant such as alumina, bauxite, calcium sulfate, clays, silica gel, zeolites, alkaline metal oxides, alkaline earth metal oxides, sulfates, or metal

halides and perchlorates. Methods for encapsulation and desiccation include, but are not limited to, those described in U.S. Patent No. 6,226,890. In addition, barrier layers such as SiO<sub>x</sub>, Teflon, and alternating inorganic/polymeric layers are known in the art for encapsulation.

5     Optical Optimization

           OLED devices of this invention can employ various well-known optical effects in order to enhance its properties if desired. This includes optimizing layer thicknesses to yield maximum light transmission, providing dielectric mirror structures, replacing reflective electrodes with light-absorbing  
10    electrodes, providing anti-glare or anti-reflection coatings over the display, providing a polarizing medium over the display, or providing colored, neutral density, or color-conversion filters over the display. Filters, polarizers, and anti-glare or anti-reflection coatings may be specifically provided over the cover or as part of the cover.

15           The invention and its advantages can be better appreciated by the following examples.

Triplet Energy Calculation Example 1

           The triplet energy of compound Inv-11 was calculated using the  
20    B3LYP/MIDI! method as implemented in the Gaussian98 (Gaussian, Inc., Pittsburgh, PA) computer program. The energies of the ground state, E(gs), and the lowest triplet state, E(ts), were calculated. The energy of each state was computed at the minimum-energy geometry for that state. The difference in energy between the two states was further modified by the following equation to  
25    give the triplet energy:  $E(t) = 0.84 \cdot (E(ts) - E(gs)) + 0.35$ . The triplet energy, E(t), of compound Inv-11 was calculated as 2.60 eV. The triplet energy of the green dopant, *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III), (Ir(ppy)<sub>3</sub>), has been calculated by this method to be 2.55 eV and measured to be 2.53 eV. The calculations predict that Inv-11 will be a suitable host for the green dopant  
30    Ir(ppy)<sub>3</sub>.

Synthetic Example 1: Preparation of Inv-11:

4,'4-Diaminooctafluorobiphenyl (Aldrich, 2.0 g, 6.1 mmol), 4-bromobiphenyl (Aldrich, 7.5 g, 32.2 mmol) palladium diacetate (150 mg, 0.7 mmol), tri-*t*-butylphosphine (0.6 mL), sodium *t*-butoxide (2.8 g, 29.2 mmol), and  
5 xylene (90 mL) were combined in a 250 mL-flask with magnetic stirring and condensor. The mixture was heated at 125 °C under a nitrogen atmosphere for 6 h. The heat was removed and after, cooling to room temperature, a solid was collected by filtration. This material was dissolved in methylene chloride and filtered. The filtrate was evaporated. The solid obtained was slurried with ligroin  
10 and then collected. This material was sublimed twice at 380 °C under vacuum (0.6 Torr) with a stream of nitrogen gas to afford Inv-11, mass spectrum *m/e*: 937.

Device Example 1

An EL device (Sample 1) satisfying the requirements of the  
15 invention was constructed in the following manner:

1. A glass substrate coated with an 85 nm layer of indium-tin oxide (ITO) as the anode was sequentially ultrasonicated in a commercial detergent, rinsed in deionized water, degreased in toluene vapor and exposed to oxygen plasma for about 1 min.
- 20 2. Over the ITO was deposited a 1 nm fluorocarbon (CF<sub>x</sub>) hole-injecting layer (HIL) by plasma-assisted deposition of CHF<sub>3</sub>.
3. A hole-transporting layer (HTL) of *N,N'*-di-1-naphthyl-*N,N'*-diphenyl-4, 4'-diaminobiphenyl (NPB) having a thickness of 75 nm was then evaporated from a tantalum boat.
- 25 4. A 35 nm light-emitting layer (LEL) of Inv-11 and a green phosphorescent dopant, *fac*-tris(2-phenylpyridinato-*N,C*<sup>2'</sup>)iridium(III), (Ir(ppy)<sub>3</sub>), 3 % wt%) were then deposited onto the hole-transporting layer. These materials were also evaporated from tantalum boats.
- 30 5. A hole-blocking layer of bis(2-methyl-quinolinolate)(4-phenylphenolate) (Al (Balq)) having a thickness of 10 nm was then evaporated from a tantalum boat.

6. A 40 nm electron-transporting layer (ETL) of tris(8-quinolinolato)aluminum (III) ( $\text{AlQ}_3$ ) was then deposited onto the light-emitting layer. This material was also evaporated from a tantalum boat.

7. On top of the  $\text{AlQ}_3$  layer was deposited a 220 nm cathode formed of a 10:1 volume ratio of Mg and Ag.

The above sequence completed the deposition of the EL device. The device was then hermetically packaged in a dry glove box for protection against ambient environment.

Samples 2, 3 and 4 were fabricated in an identical manner to Sample 1 except emitter  $\text{Ir(ppy)}_3$  was used at the level indicated in the table. Sample 5 was fabricated in an identical manner to Sample 1 except compound  $\text{Ir(ppy)}_3$  was not included. The cells thus formed were tested for luminance, efficiency and color CIE (Commission Internationale de L'Eclairage) coordinates at an operating current of 20  $\text{mA/cm}^2$  and the results are reported in Table 1.

Table 1. Evaluation Results for EL devices.

Sample	Green Dopant Level (%)	Lumiance ( $\text{cd/m}^2$ )	Efficiency (W/A)	CIE <sub>x</sub>	CIE <sub>y</sub>	Type
1	3	1201	0.040	0.327	0.600	Invention
2	6	1958	0.064	0.334	0.607	Invention
3	9	2130	0.070	0.337	0.606	Invention
4	12	2152	0.070	0.339	0.605	Invention
5	0	73	0.004	0.241	0.354	Comparison

As can be seen from Table 1, all tested EL devices incorporating the invention compound as a host material for the green phosphorescent dopant demonstrated a green color and good efficiency.

#### Device Example 2

An EL device (Sample 6) satisfying the requirements of the invention was constructed in the same manner as Sample 1, except a red phosphorescent dopant (RPD-1) was used in place of  $\text{Ir(ppy)}_3$ .

Samples 7, 8 and 9 were fabricated in an identical manner to Sample 6 except emitter RPD-1 was used at the level indicated in the table. Sample 10 was fabricated in an identical manner to Sample 6 except compound RPD-1 was not included. The cells thus formed were tested for luminance, efficiency and color CIE coordinates at an operating current of 20 mA/cm<sup>2</sup> and the results are reported in Table 2.

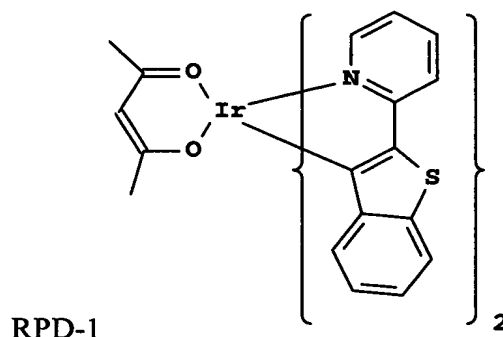


Table 2. Evaluation Results for EL devices.

Sample	Red Dopant Level (%)	Lumiance (cd/m <sup>2</sup> )	Efficiency (W/A)	CIE <sub>x</sub>	CIE <sub>y</sub>	Type
6	3	317	0.040	0.653	0.316	Invention
7	6	507	0.065	0.677	0.318	Invention
8	9	596	0.076	0.676	0.318	Invention
9	12	676	0.087	0.677	0.319	Invention
10	0	74	0.004	0.246	0.360	Comparison

As can be seen from Table 2, all tested EL devices incorporating the invention compound as a host material for the red phosphorescent dopant demonstrated a red color and good efficiency.

The entire contents of the patents and other publications referred to in this specification are incorporated herein by reference. The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

**PARTS LIST**

101	Substrate
103	Anode
105	Hole-Injecting layer (HIL)
107	Hole-Transporting layer (HTL)
109	Light-Emitting layer (LEL)
110	Hole-blocking layer (HBL)
111	Electron-Transporting layer (ETL)
113	Cathode